

VERIFICATION OF TRANSLATION

Re: U.S. PATENT APPLICATION SERIAL NO. 60/531,496

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hereby declare that I am the translator of the
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Signature of translator



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Applicant(s)

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Title

Heat resistant label applicable under high temperature

LICENSE FOR FOREIGN FILING UNDER

Title 35, United States Code, Section 184

Title 37, Code of Federal Regulations, 5.11 & 5.15

GRANTED

HEAT RESISTANT LABEL APPLICABLE UNDER HIGH TEMPERATURE

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

5 The present invention relates to compositions for heat-resistant labels that are attachable to high-temperature products (300°C or higher), heat-resistant labels, products with the labels attached, and methods for producing the labels.

10 DESCRIPTION OF THE RELATED ART

 In various industrial fields, such as food, machinery and chemicals, a label on which symbols, letters, patterns, etc., have been printed, i.e., a patterned label, is attached to products or their packaging materials to control the production process. A typical example of such
15 process control is a system utilizing labels on which a bar-code is printed. In a bar-code control system, data such as production conditions, production managers, production period, destination, and product price are read from the bar-code label by a bar-code reader to control production, sales, and distribution.

20 The bar-code labels that are currently in wide use are made by producing a resin or paper label having poor heat resistance, and then applying an adhesive made of acrylic resin or the like to it. However, because both the label and the adhesive decompose and evaporate at temperatures of 300°C or higher, they cannot be used in industries requiring
25 high-temperature processing, such as ceramics, metals, and the like. Japanese Patent No. 2614022 discloses heat-resistant labels but does not disclose attaching the labels at high temperatures. Japanese Unexamined Patent Publication No. 2003-126911 discloses labels to be subjected to a heating process in which an aluminum coil is baked but
30 discloses in Comparative Example 3 in the specification that the information on the label becomes unclear unless the attachment temperature is 150°C or lower.

 Therefore, in the metal mining industry, labels for product control are attached to metal products after the melted and formed metal

is cooled to a temperature (generally, near room temperature) in the range in which the labels can be attached. The same applies to the ceramics and glass industries, and other industries requiring high-temperature processing.

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BRIEF DESCRIPTION OF THE INVENTION

Attaching labels to metal products after cooling the temperature thereof to near room temperature requires a cooling period, cooling energy, and a cooling place. In order to efficiently produce metal products, product control needs to be started sooner by attaching labels to the products at higher temperatures. Accordingly, an object of the present invention is to provide heat-resistant labels attachable under high temperature conditions.

The inventors carried out extensive research to achieve the above-mentioned objects in view of the problems of the prior art. As a result, they found that heat-resistant labels having as a sticking layer a hardened coating film made of a composition comprising a polymetallocarbosilane resin (A), a silicone resin (B), a solvent (C), and, as needed, an inorganic powder (D) can be attached at temperatures of 300°C or higher. The inventors further found that heat-resistant labels with an aluminum foil layer on one side of a support can be attached at temperatures of 700°C or higher, and the present invention has been accomplished based on these findings.

The present invention thus relates to the following compositions, heat-resistant labels, products with heat-resistant labels attached, and methods for producing the products.

Item 1. A composition for a heat-resistant label comprising a polymetallocarbosilane resin (A), a silicone resin (B), and a solvent (C), wherein the polymetallocarbosilane resin (A) and the silicone resin (B) are mixed in a weight ratio of about 1 to about 9 to about 9 to about 1.

Item 2. A composition for a heat-resistant label further comprising an inorganic powder (D) in an amount of about 0.0001 to about 80% by weight.

Item 3. A composition for a heat-resistant label according

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to Item 1 or 2, wherein the polymetallocarbosilane resin (A) and the silicone resin (B) are mixed in a weight ratio of about 3 to about 7 to about 8 to about 2.

Item 4. A composition for a heat-resistant label according
5 to any one of Items 1 to 3, wherein the weight-average molecular weight of the polymetallocarbosilane resin (A) is about 500 to about 10000.

Item 5. A composition for a heat-resistant label according to any one of Items 1 to 4, wherein the weight-average molecular weight of the silicone resin (B) is about 200 to about 5000000.

10 Item 6. A composition for a heat-resistant label according to any one of Items 1 to 5, wherein the polymetallocarbosilane resin (A) is at least one member selected from the group consisting of polytitanocarbosilane resins and polyzirconocarbosilane resins.

Item 7. A heat-resistant label comprising a support and a
15 sticking layer, the sticking layer being obtained by applying a composition of any one of Items 1 to 6 onto one side of the support and evaporating the solvent contained in the composition to form a hardened coating film.

Item 8. A heat-resistant label according to Item 7, wherein the sticking layer is about 5 μm to about 100 μm thick.

20 Item 9. A heat-resistant label according to Item 7 or 8, wherein the support is about 5 μm to about 100 μm thick.

Item 10. A heat-resistant label according to any one of Items 7 to 9, wherein the support is any one of an aluminum foil, stainless steel foil, or copper foil.

25 Item 11. A heat-resistant label according to any one of Items 7 to 10 having a heat-resistant label base layer on the other side of the support.

Item 12. A heat-resistant label according to Item 11, wherein the label base layer is about 0.5 μm to about 100 μm thick.

30 Item 13. A heat-resistant label according to Item 11 or 12, wherein the label base layer is a cured coating film obtained by crosslinking the resins of the composition of any one of Items 1 to 6.

Item 14. A heat-resistant label according to any one of Items 11 to 13 comprising an identification part on the label base layer.

35 Item 15. An article to which a heat-resistant label of any

one of Items 7 to 14 is attached using a cured sticking layer.

Item 16. A method for producing a heat-resistant label, the method comprising the steps of:

- 5 applying a composition of any one of Items 1 to 6 to one side of a support; and
- drying the applied composition to form a hardened coating film.

Item 17. A production method according to Item 16, wherein the applied composition is dried at about 50°C to about 240°C.

- 10 Item 18. A production method according to Item 16 or 17, comprising, prior to the step of applying a composition of any one of Items 1 to 6 to one side of a support, the steps of:

- applying a composition for a heat-resistant label base layer to the other side of the support; and
- 15 drying the applied composition to form a cured coating film.

Item 19. A production method according to any one of Items 16 to 18, wherein the composition for a label base layer is a composition of any one of Items 1 to 6.

- 20 Item 20. A method for producing an article with a heat-resistant label attached, the method comprising the step of attaching a heat-resistant label of any one of Items 7 to 14 to an article at about 300°C to about 670°C.

- 25 Item 21. A heat-resistant label comprising a support and an aluminum foil layer or aluminum-alloy foil layer being laminated on one side of the support.

Item 22. A heat-resistant label according to Item 21, wherein the aluminum foil layer or aluminum-alloy foil layer is laminated on the support through an adhering layer.

- 30 Item 23. A heat-resistant label according to Item 21 or 22, wherein the aluminum foil layer or aluminum-alloy foil layer has a thickness of 5 μm to 100 μm .

Item 24. A heat-resistant label according to any one of Items 21 to 23, wherein the support is a stainless steel foil, copper foil, or iron foil.

- 35 Item 25. A heat-resistant label according to any one of Items

21 to 24, comprising a heat-resistant label base layer on the other side of the support.

Item 26. A heat-resistant label according to Item 25, wherein the label base layer has a thickness of about 0.5 μm to about 100 μm .

Item 27. A heat-resistant label according to Item 25 or 26, wherein the label base layer is a cured coating film obtained by crosslinking the resins of a composition of any one of Items 1 to 6.

Item 28. A heat-resistant label according to any one of Items 25 to 27, comprising an identification part on the label base layer.

Item 29. An article to which a heat-resistant label of any one of Items 21 to 28 is attached.

Item 30. A method for producing an article with a heat-resistant label attached, the method comprising the step of attaching a heat-resistant label of any one of Items 21 to 29 to an article at about 300°C to about 1100°C.

DETAILED DESCRIPTION OF THE INVENTION

The compositions for heat-resistant labels of the present invention comprise a polymetallocarbosilane resin (A), a silicone resin (B), and a solvent (C). The polymetallocarbosilane resin (A) and the silicone resin (B) are mixed in a weight ratio of about 1 to about 9 to about 9 to about 1.

The heat-resistant label of the invention comprises a polymetallocarbosilane resin (A), and thus can be attached at high temperatures. The polymetallocarbosilane resin (A) has a crosslinked structure obtained by, for example, reacting polycarbosilane with metal alkoxide. Examples of the above-mentioned metal include titanium, zirconium, molybdenum, chromium, etc., and among these titanium and zirconium are preferable. Preferred examples of the polymetallocarbosilane resin are polytitanocarbosilane resins, polyzirconocarbosilane resins, etc. As a mixture comprising the polytitanocarbosilane resin, for example, a "Tyranno coat VS-100", "Tyranno coat VN-100", etc. manufactured by Ube Industries, Ltd., can be used. The weight-average molecular weight of the polymetallocarbosilane resin is preferably about 500 to about 10000,

and more preferably about 700 to about 3000.

In the invention, the silicone resin (B) has a polyorganosiloxane structure in its molecule. Examples of silicone resins include straight silicone resins, modified silicone resins, etc. Such silicone resins may be used in combination. Among the above, straight silicone resins are preferred. Such resins may be used as is or in the form of a solution in a solvent. In order to facilitate the process of applying the resin onto a support during the preparation of the label, the resin is preferably used in the form of solution in a solvent.

The weight average molecular weight of the silicone resin (B) is generally about 200 to about 5000000, preferably about 1000 to about 1000000.

A straight silicone resin includes an organopolysiloxane comprising a hydrocarbon group as a main organic group. The organopolysiloxane may contain a hydroxyl group. Examples of the foregoing hydrocarbon groups include aliphatic hydrocarbon groups and aromatic hydrocarbon groups. Preferred among the above are C_{1-5} aliphatic hydrocarbon groups and C_{6-12} aromatic hydrocarbon groups. Such hydrocarbon groups may be used singly or in combination.

Examples of the C_{1-5} aliphatic hydrocarbon groups include methyl, ethyl, propyl, butyl, pentyl, vinyl, allyl, propenyl, butenyl, and pentenyl groups. Examples of the C_{6-12} aromatic hydrocarbon groups include phenyl, methylphenyl, ethylphenyl, butylphenyl, tertiary butylphenyl, naphthyl, styryl, allylphenyl, and propenylphenyl groups.

The straight silicone resin may be obtained by hydrolyzing one or more silane compounds such as a chlorosilane or alkoxysilane comprising the foregoing aliphatic hydrocarbon group or aromatic hydrocarbon group, and then condensing the hydrolysis products, or by hydrolyzing a mixture of the foregoing silane compound with tetrachlorosilane or tetraalkoxysilane, and then co-condensing the hydrolysis product.

Examples of the foregoing chlorosilane compounds include methyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane, methylethyldichlorosilane, vinylmethyldichlorosilane, vinyltrichlorosilane, phenyltrichlorosilane, diphenyldichlorosilane,

methylphenyldichlorosilane, vinylphenyldichlorosilane, etc.

Examples of the foregoing alkoxysilane compounds include methyltrimethoxysilane, dimethyldiethoxysilane, trimethylmethoxysilane, vinylmethylmethoxysilane, vinyltributoxysilane, phenyltriethoxysilane, diphenyldimethoxysilane, methylphenyldipropoxysilane, vinylphenyldimethoxysilane, etc.

The modified silicone resin is an organopolysiloxane containing an organic group other than a hydrocarbon group. Examples of the modified silicone resin include methoxy-containing silicone resins, ethoxy-containing silicone resins, epoxy-containing silicone resins, alkyd resin-modified silicone resins, acrylic resin-modified silicone resins, polyester resin-modified silicone resins, epoxy resin-modified silicone resins, etc.

These modified silicone resins can be obtained by, for example, reacting the hydroxyl group of the foregoing straight silicone resin with an organic compound having a functional group reactive to the hydroxyl group, such as carboxyl, acid anhydride, hydroxyl, aldehyde, epoxy, and chloride groups; by copolymerizing a straight silicone resin containing an unsaturated hydrocarbon group, such as a vinyl group, with a compound having an unsaturated double bond; by hydrolyzing a modified silane compound obtained by the reaction of the foregoing silane compound with another organic compound so that it undergoes condensation or co-condensation, or the like. The organic compound to be reacted may be a low molecular weight compound or a high molecular weight compound such as a resin.

Examples of the silicone resin (B) include dimethylpolysiloxane, methylphenylpolysiloxane, diphenylmethylphenylsilicone resins, etc.

The weight ratio of the polymetalloccarbosilane resin (A) : the silicone resin (B) is preferably about 1:9 to about 9:1, and more preferably about 3:7 to about 8:2. The composition obtained by mixing these two resins within such a range is favorable for label attachment under high temperature conditions. The total amount of both resins is preferably about 5 to about 50% by weight, and more preferably about 10 to about 45% by weight, of the composition of the invention.

In the invention, the solvent (C) has a function of dissolving or dispersing components in the composition to adjust the viscosity thereof. Usable as the solvent (C) are, for example, toluene, xylene, cellosolve acetate, ethyl acetate, butyl carbitol, MEK (methyl ethyl ketone), MIBK (methyl isobutyl ketone), etc. Among these, xylene and toluene are preferable. The proportion of the solvent (C) is not limited insofar as a heat-resistant label can be produced using the composition of the invention. Thus, the proportion of the solvent (C) can be appropriately adjusted in such a manner that the viscosity of the composition of the invention is suitable for application to the support and drying. The proportion of solvent (C) is usually about 15 to about 70% by weight, and preferably about 20 to about 50% by weight, of the composition of the invention.

In the invention, the heat-resistance of the heat-resistant label can be enhanced by mixing an inorganic powder (D) since thermal expansion and shrinkage of the heat-resistant label can be thereby reduced. Thus, an inorganic powder (D) is preferably mixed with the composition of the invention. The label base layer can be colored by using a color pigment as the inorganic powder (D). Such inorganic powders (D) can be used singly or in combination. The particle diameter of the inorganic powders (D) is preferably about 0.01 μm to about 200 μm , and more preferably about 0.1 μm to about 100 μm . The inorganic powder (D) is not limited in shape. Single-crystal inorganic fibers of high aspect ratio, such as potassium-titanate whiskers, can be mentioned as an example of the inorganic powder (D). The proportion of inorganic powder (D) is usually about 0.0001 to about 80% by weight, and preferably about 1 to about 65% by weight, of the composition of the invention.

An inorganic pigment is used preferably as the inorganic powder (D). For example, usable are white substances, such as silica, titanium dioxide, alumina, zinc, zirconia, mica, calcium oxide, zinc sulfide-barium sulfate (lithopone), etc. Moreover, usable are metal compounds, such as carbonates, nitrates, sulfates, etc., which are oxidized to form such white substances in a heat treatment during the production of the heat-resistant label. Also, usable as the inorganic powder (D) are reddish-brown substances containing metal ion such as

iron, copper, gold, chromium, selenium, zinc, manganese, aluminum, tin, etc. (e.g., zinc oxide-iron oxide-chromium oxide, manganese oxide-alumina, chromium oxide-tin oxide, iron oxide, etc.); blue substances containing metal ion such as manganese, chromium, aluminum, cobalt, copper, iron, zirconia, vanadium, etc. (e.g., cobalt oxide-aluminum oxide, cobalt oxide-aluminum oxide-chromium oxide, cobalt oxide, zirconia-vanadium oxide, chromium oxide-divanadium pentoxide, etc.); black substances containing metal ion such as iron, copper, manganese, chromium, cobalt, aluminum, etc. (e.g., copper oxide-chromium oxide-manganese oxide, chromium oxide-manganese oxide-iron oxide, chromium oxide-cobalt oxide-iron oxide-manganese oxide, chromate, permanganate, etc.); yellow substances containing metal ion such as vanadium, zinc, tin, zirconium, chromium, titanium, antimony, nickel, praseodymium, vanadium, etc. (e.g., titanium oxide-antimony oxide-nickel oxide, titanium oxide-antimony oxide-chromium oxide, zinc oxide-iron oxide, zirconium-silicon-praseodymium, vanadium-tin, chromium-titanium-antimony, etc.); green substances containing metal ion such as chromium, aluminum, cobalt, calcium, nickel, zinc, etc. (e.g., titanium oxide-zinc oxide-cobalt oxide-nickel oxide, cobalt oxide-aluminum oxide-chromium oxide-titanium oxide, chromium oxide, cobalt-chromium, alumina-chromium, etc.); pink substances containing metal ion such as iron, silicon, zirconium, aluminum, manganese, etc. (e.g., aluminum-manganese, iron-silicon-zirconium, etc.). Among these, preferable are titanium dioxide, alumina, zinc oxide-iron oxide-chromium oxide, titanium oxide-antimony oxide-nickel oxide, titanium oxide-antimony oxide-chromium oxide, zinc oxide, iron oxide, zinc oxide-iron oxide-chromium oxide, titanium oxide-zinc oxide-cobalt oxide-nickel oxide, cobalt oxide-aluminum oxide-chromium oxide, cobalt oxide-aluminum oxide, cobalt oxide-aluminum oxide-chromium oxide, copper oxide-chromium oxide-molybdenum oxide, copper oxide-chromium oxide-manganese oxide, copper oxide-manganese oxide-iron oxide.

A dispersant (E) is preferably mixed into the composition for heat-resistant labels of the invention. This is because the dispersion rate is improved by mixing a dispersant, thereby facilitating preparation of the composition. Usable as the dispersant (E) are aliphatic polyvalent

carboxylic acids, amine salts of polyester acids, long-chain amine salts of polycarboxylic acids, amine salts of polyether ester acids, amine salts of polyether phosphates, polyether phosphates, amide amine salts of polyester acids, etc. The dispersant (E) is generally used in a proportion of about 0.01 parts by weight to about 5 parts by weight, preferably about 0.1 parts by weight to about 2 parts by weight of the composition of the invention.

Additives, such as crosslinking agents, plasticizers, etc., can also be added as needed to the composition for heat-resistant labels of the invention within ranges that do not adversely affect the effects of the invention, in addition to the polymetalloccarboxilane resin (A), the silicone resin (B), the solvent (C), the inorganic powder (D), and the dispersant (E).

Examples of crosslinking agents include boric acid compounds, organometallic compounds, etc. Boric acid compounds are compounds containing a boric acid residue in its molecule, and include boric acids, borates, borate esters, etc. Boric acids include orthoboric acid, metaboric acid, anhydrous boric acid, etc. Borates include sodium borate, potassium borate, magnesium borate, calcium borate, zinc borate, aluminum borate, etc. Borate esters include methyl borate, ethyl borate, butyl borate, octyl borate, dodecyl borate, etc. Among such compounds, orthoboric acid is particularly preferable.

Examples of organometallic compounds include organonickel compounds, organoiron compounds, organocobalt compounds, organomanganese compounds, organotin compounds, organolead compounds, organozinc compounds, organoaluminum compounds, organotitanium compounds, etc., and among these, chelate compounds are preferable. Crosslinking agents are preferably mixed in an amount such that the amount of metal contained in the crosslinking agent is about 0.05 parts by weight to about 10 parts by weight, preferably about 0.1 parts by weight to about 5 parts by weight, per 100 parts by weight of the total amount of the resin (A) and the resin (B).

Examples of plasticizers include aliphatic esters, aromatic esters, phosphate esters, etc. Specific examples of aliphatic esters include methyl laurate, butyl oleate, diethylene glycol dilaurate,

di(2-ethylbutoxyethyl) adipate, etc. Specific examples of aromatic esters include dimethyl phthalate, dioctyl phthalate, di(2-ethylhexyl) phthalate, dilauryl phthalate, oleyl benzoate, phenyl oleate, etc. Specific examples of phosphate esters include tricresyl phosphate, trioctyl phosphate, etc. The addition of such plasticizers can provide a further improvement in the flexibility of the label base layer.

The composition of the invention can be prepared by mixing and dispersing the above-mentioned components. The components can be dispersed by a dispersion mill, such as a bead mill, a disper ball mill, a sand mill, a roll mill, etc. The grain size of the dispersion in the distributor is preferably about 0.01 μm to about 200 μm , and more preferably about 0.1 μm to about 20 μm .

The composition of the invention can be used as a starting material for the sticking layer of the heat resistant label of the invention which is suitable for use at temperatures of about 300°C to about 670°C. More specifically, the sticking layer is formed by applying the composition of the invention to one side of a support, and drying the applied composition until the solvent in the composition is removed so as to form a hardened coating film. The composition of the invention can also be used as a starting material for forming the label base layer of the heat-resistant label of the invention. More specifically, the label base layer is formed by applying the composition of the invention to one side of the support, and drying the applied composition at a temperature at which the resins in the composition are crosslinked in such a manner as to form a cured coating film.

In this specification, a hardened coating film represents a film which is obtained by drying the composition of the invention until the solvent in the composition is substantially removed, and which can function as a sticking layer at temperatures of 300°C or higher. Crosslinking of the resins may proceed in such a manner that functionality as the sticking layer is demonstrated. Any remaining solvent might raise the possibility of ignition under high temperature conditions. Therefore, the amount of solvent remaining in the hardened coating film is usually about 0.1% by weight or less, preferably 0.0001% by weight or less. Crosslinking of the resins in the composition may occur in the drying

process for removing the solvent. In the case of excessive crosslinking thereof, the film is cured, and thus the sticking ability is lost under high temperature conditions. Therefore, it is important to conduct the drying process under the drying conditions for forming the hardened coating film where the solvent is removed and the sticking function is maintained even under high temperature conditions, even if crosslinking proceeds.

The cured coating film is useful for the label base layer of the heat-resistant label. For example, it can be used as a label base layer of the following heat-resistant label of the invention. A label is known whose support, such as a stainless steel foil or the like, is attached to a target by welding (spot welding, etc.); however the above-mentioned cured coating film can also be used as a label base layer that is attached by welding.

In this specification, a cured coating film represents a film which is obtained by drying the composition of the invention until the solvent in the composition is at least substantially removed and the film is cured to an extent that the film does not adhere to a label attaching machine and, if it is used as a label base layer with an identification part, the identification part is kept, at temperatures of 300°C or higher in the attachment process. In order to avoid the film from sticking to the label attaching machine, the film needs to be cured by proceeding crosslinking. Thus, the heating conditions for forming the cured coating film need to be more severe than those for the hardened coating film.

The heat-resistant label of the invention is suitable for attachment to a target having temperatures of about 300°C or higher. Further, the heat-resistant labels of the invention are roughly classified into heat-resistant labels which are suitable for use at about 300°C to about 670°C, and those suitable for use at about 300°C to about 1100°C, and more preferably at about 670°C to about 1100°C. In this specification, the former is sometimes referred to as "heat-resistant label 1" and the latter as "heat-resistant label 2".

The heat-resistant label 1 of the invention is described. The heat-resistant label 1 has a sticking layer, which is made of a hardened coating film obtained by applying the above-mentioned composition of the invention to one side of the support, and drying the solvent of the

applied composition. The heat-resistant label 1 can be provided with a heat-resistant label base layer on the other side of the support, on which no sticking layer is provided. When a label base layer is not provided, an identification part, such as a bar code or the like, can be provided directly onto the support.

The support of the heat-resistant label 1 of the invention is made of a film-like and heat-resistant material, and a metal foil is preferable. Minute pores may be formed in the support. Forming pores makes it easy to evacuate gas produced when resins contained in the sticking layer and label base layer laminated on the support decompose at high temperatures, thereby suppressing expansion of the label base layer. A support made of the same material as the label attaching target gives the label a comparatively high resistance against thermal expansion and shrinkage. Examples of metal foils include aluminum foil, stainless steel foil, copper foil, iron foil, etc. Among these, the aluminum foil is preferably used as the support. The thickness of the support is usually about 5 μm to about 100 μm , preferably about 10 μm to about 50 μm , and more preferably about 10 μm to about 40 μm . When the thickness of the support is within such a range, breakage of the label is suppressed due to further reduced thermal expansion or thermal contraction, and furthermore, due to the flexibility, the label can be attached in accordance with the shape of the target.

Examples of aluminum foils include JIS alloys 1N30, 1085, 1N90, 1N99, 3003, 3004, 5052, 8079, and 8021, etc., with 1N30 being preferable.

Examples of stainless steel foils include martensite-based (SUS410, SUS440), ferrite-based (SUS430, SUS444), austenite-based (SUS304, SUS316), two-sided based (SUS329J1, SUS329J4L) foils, SUS630, and SUS631, etc.

JIS SPHC, SPCC, SECC, SGCC, SZACC, SA1C, etc. can be used as other metals, and among these, SPHC and SPCC Standard are preferable.

Easily available commercial metal foils can be used as the above-described supports.

In the heat-resistant label 1 of the invention, the sticking layer is the above-described hardened coating film. More specifically,

such a film is obtained by drying the composition of the invention until the solvent in the composition is at least substantially removed, and serves as a sticking layer under high temperature conditions of 300°C or higher.

5 The temperature and period for drying the composition of the invention to form the sticking layer are not limited insofar as the composition of the invention is dried and the resultant endproduct serves as a sticking layer under high temperature conditions. Thus, the temperature and period are appropriately changed according to the
10 thickness and the solvent content of the coating film obtained by applying the composition of the invention, and material and the thickness of the support. For example, drying may be carried out with a convection oven at about 50°C to about 240°C, preferably at about 80°C to about 200°C, for about 1 minute to about 60 minutes, and preferably about 1 minute
15 to about 20 minutes. The drying period can be suitably adjusted according to the flow of hot air.

 The thickness of the sticking layer after drying is usually about 5 μm to about 100 μm , preferably about 10 μm to about 60 μm . When the dry film thickness of the sticking layer is within such a range,
20 the sticking layer is strongly stuck to the target, thereby inhibiting cohesion failure of the sticking layer.

 The heat-resistant label 1 of the invention has a sticking layer on one side of the support, and a heat-resistant label base layer can be formed on the other side of the support. Any conventionally used
25 or reported films obtained by drying compositions for the formation of the label base, such as a composition comprising, for example, a silicone resin, inorganic powder, and organic solvent, can be used as the label base layer insofar as it can withstand temperatures of 300°C or higher. A cured coating film obtained by drying the composition of the invention
30 can also be used as the label base layer. The label base layer can be formed by applying the composition of the invention to one side of the support and drying the applied composition until the solvent of the composition is substantially removed and the resins in the composition are crosslinked, so as to form a cured coating film.

35 When the composition of the invention is used for forming

the label base layer, the temperature and period for drying the composition of the invention are not limited insofar as the composition of the invention is dried and the resultant end product serves as the label base layer under high temperature conditions. Thus, the heating temperature and period are appropriately varied according to the thickness and solvent content of the coating film obtained by applying the composition of the invention to the support, and the material and thickness of the support. For example, heating may be carried out with a convection oven at about 245°C to about 500°C, preferably at about 250°C to about 400°C for about 1 minute to about 40 minutes, preferably about 2 minutes to about 20 minutes. The drying period can be suitably adjusted according to the flow of hot air. The thickness of the label base layer after it is dried is generally about 0.5 μm to about 100 μm , and preferably about 1 μm to about 60 μm .

To produce the heat-resistant label 1 with the label base layer obtained by curing the composition of the invention, the label base layer is first formed on one side of the support, and subsequently the sticking layer is formed on the other side of the support. When the label base layer is formed after the sticking layer, both the layers are made into a cured coating film due to the severer heating conditions for forming the label base layer than those for forming the sticking layer. In such a case, the heat-resistant label cannot be attached under high temperature conditions. When the label base layer is formed using the conventional composition for forming the label base, the order of forming the layers can be suitably determined considering the drying conditions applied to this composition and the sticking layer.

The method for manufacturing the heat-resistant label 1 of the invention comprises: applying the composition of the invention to one side of the support; and drying the applied composition to form a hardened coating film.

The composition of the invention is applied to one side of the support by, for example, a printing method such as screen-printing, etc., a roll coater method, gravure roll coater method, doctor blade method, bar coater method, etc. Screen-printing, gravure roll coating, and bar coating methods are preferable as application methods. The

composition of the invention is applied to the support, and dried to form a hardened coating film (sticking layer). The drying conditions are the same as those for the sticking layer.

5 The method for producing the heat-resistant label 1 with the label base layer of a cured coating film obtained by curing the composition of the invention comprises, prior to applying the composition of the invention to one side of the support in the above-mentioned production method: applying the composition for the heat-resistant label base layer to the other side of the support; and drying the applied composition
10 to form a cured coating film.

When the composition of the invention is used as a composition for a heat-resistant label base layer, the step of applying the composition for the heat-resistant label base layer may be carried out in the same manner as the above-described step of applying the composition of the
15 invention. The step of curing the composition of the invention by drying is carried out under the same conditions as the above-described conditions for forming the label base layer.

A conventional composition for a label base layer may be used as the composition for the heat-resistant label base formation. In this
20 case also, the conventional composition can be applied in the same manner as the above-described step of applying the composition of the invention to one side of the support. In the curing step, the drying conditions can be suitably varied according to the composition used.

The heat-resistant label 2 of the invention is now described.
25 The heat-resistant label 2 has a support and an aluminum foil or aluminum-alloy foil layer on one side of the support, and is suitable for use at about 300°C to about 1100°C, preferably 670°C to about 1100°C, and more preferably about 700°C to about 1000°C. An adhering layer for adhering the aluminum foil or aluminum-alloy foil layer may be provided
30 between the support and the aluminum foil or aluminum-alloy foil layer. The heat-resistant label 2 is stuck to the attachment target when the aluminum foil or aluminum-alloy foil layer melts under high temperature conditions. A label having an aluminum layer that is formed by thermally
35 spraying aluminum onto the support surface does not stick to the target, since the aluminum layer does not melt at the temperature of the attachment

target. This is because the melting temperature of the layer obtained by thermal spraying is elevated by oxidization of the surface, whose area is increased by thermal spraying.

A film-like material which does not melt within the temperature range desirable for the label is usable for the support of the heat-resistant label 2, and a metal foil is preferable. A support made of the same material as the label attaching target gives the label further improved resistance against thermal expansion and shrinkage. Examples of metal foils include stainless steel foil, copper foil, iron foil, etc. Among these, stainless steel foil is preferable. The thickness of the support is usually about 5 μm to about 100 μm , preferably about 10 μm to about 50 μm , and more preferably about 10 μm to about 40 μm . When the thickness of the support is within such a range, breakage of the label is sufficiently suppressed due to further reduced thermal expansion or thermal shrinkage, and furthermore, due to the flexibility, the label can be attached in accordance with the shape of the target. Examples of stainless steel foils are the same as in the support of the heat-resistant label 1. The same applies to the other metal foils.

The heat-resistant label 2 can be attached when the aluminum foil layer or aluminum-alloy foil layer melts at high temperatures. Accordingly, the aluminum foil layer is formed onto only one side of the support. The thickness of the aluminum foil layer or aluminum-alloy foil layer is usually about 1 μm to about 300 μm , preferably about 10 μm to about 100 μm . Examples of aluminum foils include, JIS alloys 1N30, 1085, 1N90, 1N99, 3003, 3004, 5052, 8079, and 8021, etc., and among these, 1N30 is preferable. In aluminum-alloy foil, the proportion of aluminum in the alloy is usually 1% by weight to 99% by weight, and preferably 5% by weight to 99% by weight. Any aluminum-alloy can be used insofar as it is alloy of aluminum and another metal(s), and melts at temperatures favorable for the use of the heat-resistant label 2. The melting temperature can be adjusted by alloying. For example, usable are aluminum-alloy foils of aluminum with at least one metal selected from the group consisting of zinc, tin, indium, copper, nickel, and silver. Among these, alloys of aluminum with zinc and alloys of aluminum with tin are preferable.

The aluminum foil layer or aluminum-alloy foil layer is laminated on the support by, for example, a method of adhering the aluminum foil layer or aluminum-alloy foil layer to the support with an adhering layer composed of a resin, etc.

5 Through such an adhering layer, the aluminum foil layer or aluminum-alloy foil layer is adhered to the support. Any adhering layer may be used without limitation insofar as the aluminum foil layer or aluminum-alloy foil layer is adhered to the support, until the aluminum foil layer or aluminum-alloy foil layer melts and adheres to the support
10 and target. In general, examples of an adhesive forming the adhering layer include: polyolefin-based resins such as polyethylene (e.g., low-density and high-density polyethylenes), polypropylene, polybutene, polyisobutylene, isobutylene maleic anhydride copolymers, polyvinyl acetate, polypropylene chloride, polyvinylidene chloride, polyvinyl
15 ether, etc.; acrylate-based resins such as polymethylmethacrylate, polyacrylic acid, polymethacrylate, polyacrylamide, etc.; polyester-based resins such as polyethylene terephthalate, polybutylene terephthalate, polyethylene naphthalate, polycyclohexane dimethyleneterephthalate, etc.; petroleum-based resins such as
20 polycyclopentadiene, etc.; silicone-based resins such as straight silicone resins, modified silicone resins, etc.; phenol-based resins such as 100% phenol resin, novolak-type phenol resins, resol-type phenol resins, etc.; modified alkyd resins such as rosin-modified alkyd resins, phenol-modified alkyd resins, styrene alkyd resins, silicone-modified
25 alkyd resins, etc. Such resins can be used singly or in combination. If necessary, the resins can be dissolved or dispersed in a solvent. In addition to these resins, metal foils with a low melting point can be used. Resins that evaporate or decompose with heat near the temperature at which the aluminum foil or aluminum-alloy foil layer adheres to the
30 support are preferable as the adhesive constituting the adhering layer. Additives, etc. may be suitably added to the resin adhesives in addition to these adhesives.

It is preferable that the adhering layer has sufficient adhering property so that the aluminum foil or aluminum-alloy foil layer
35 does not peel off the support. In the case of a resin adhesive, the thickness

of the layer after the solvent is removed is usually about 0.1 μm to about 50 μm , preferably about 2 μm to about 10 μm . A thin adhering layer is suitable for evaporating and decomposing the resin adhesive.

The aluminum foil or aluminum-alloy foil layer may be adhered to the support using the resin adhesive as follows: the above-mentioned adhesive (to which a solvent is added, as needed) is applied to the support, followed by drying, and then the aluminum foil or aluminum-alloy foil layer may be adhered to the support; or the adhesive is applied to the aluminum foil or aluminum-alloy foil layer, followed by drying, and then the support may be adhered thereto. These methods are preferable in that the solvent in the adhesives is easily removed by drying. Alternatively, the following processes may be employed: the adhesive is applied to the support, and then the aluminum foil layer or aluminum-alloy foil layer is adhered to the support with the adhesive, followed by drying; or the adhesive is applied to the aluminum foil layer or aluminum-alloy foil layer, and then the support may be adhered to the adhering metal foil with the adhesive, followed by drying. Also, usable is a process comprising: sandwiching a resin film between the support and the aluminum foil layer or aluminum-alloy foil layer, and then compressing the same while heating at a temperature at which the resin is adhered.

Methods for applying the adhesive to the support and the aluminum foil layer or aluminum-alloy foil layer are not limited, and in general printing methods such as screen-printing, etc.; roll coater methods, gravure roll coater methods, doctor blade methods, bar coater methods, etc. are usable. The adhesive is dried until the solvent is substantially removed, and the drying temperature, drying period, etc. can suitably vary according to the adhesive used.

Metal foil with a low melting point may be used as the adhesive by sandwiching the metal foil between the support and the aluminum foil layer or aluminum-alloy foil layer to form a laminate, and heating the laminate at a temperature at which the metal sandwiched melts.

The heat-resistant label 2 of the invention has an aluminum foil layer or aluminum-alloy foil layer on one side of the support, and can be provided with a heat-resistant label base layer on the other side. Any films obtained by drying a conventionally used or reported composition

for forming the label base, such as a composition comprising a silicone resin, inorganic powder, and organic solvent, etc., can be used as the label base layer insofar as the label base layer can withstand a temperature favorable for the use of the heat-resistant label 2 (about 300°C to about 1100°C). A cured coating film obtained by drying the composition of the invention can be used at 1100°C, and thus is preferable as a label base layer. In this case, the label base layer can be formed by applying the composition of the invention to one side of the support, and drying the applied composition to form a cured coating film at a temperature at which the solvent in the composition is substantially removed and the resin in the composition is crosslinked. The label base layer is applied to the support in the same manner as in the heat-resistant label 1.

After applying the composition of the invention to the support, the applied composition is cured by drying. The heating temperature and period are not limited insofar as the solvent contained in the composition of the invention is removed, and are appropriately varied according to the thickness and solvent content of the coating film obtained by applying the composition of the invention to the support, and the material and thickness of the support. For example, heating may be carried out with a convection oven at about 245°C to about 500°C, preferably at about 250°C to about 400°C for about 1 minute to about 40 minutes, preferably about 2 minutes to about 20 minutes. The drying period can be suitably adjusted according to the temperature or flow of hot air. The thickness of the label base layer after drying is generally about 0.5 μm to about 100 μm , preferably about 1 μm to about 60 μm .

The label base layer may be formed on a support before the adhesive layer, or the aluminum foil layer or aluminum-alloy foil layer is laminated thereon, or may be formed on a support after the adhesive layer and the aluminum foil layer or aluminum-alloy foil layer have been laminated thereon.

The heat-resistant labels 1 and 2 have the following points in common. The use of a colored label base layer (e.g., a label base layer comprising inorganic colored powder) permits product management by color classification of the products, if such product management is desired, which eliminates the necessity of having an identification part.

However, for more precise product management, it is preferable to provide an identification part on the label base layer. Providing an identification part allows the heat-resistant label to be used as a data carrier. Thus, various information can be given to a product by attaching the label provided with an identification part to the product. When the heat-resistant label 1 or 2 is provided with no label base layer, the identification part is provided on the other side of the support i.e., the side which is not stuck to the target.

The identification part is usually formed by printing patterns or images, such as characters or symbols (bar codes, etc.), onto the label base layer using known heat-resistant inks. Labels provided with such identification parts can be used as data carrier labels, typified by bar-code labels. Examples of identification parts include any identification codes such as 1-dimensional bar codes of the UPC, JAN (EAN), CODE39, CODE128, ITF, NW-7, etc.; 2-dimensional codes of the QR codes, Micro QR codes, etc.; and characters. Among these, 1-dimensional and 2-dimensional bar codes are preferable.

Inks capable of withstanding a high-temperature process, i.e., 300°C or higher, are used as the above-mentioned heat-resistant ink. Heat-resistant inks containing carbon, a metal oxide, etc. as a color pigment are particularly preferable. Examples of metal oxides for use in the heat-resistant inks include oxides of metals such as iron, cobalt, nickel, chromium, copper, manganese, titanium, aluminum, etc. These can be used singly or mixtures thereof. These metal oxides are supplied in the form of a powder, and the particle size is usually about 0.01 μm to about 50 μm , preferably about 0.1 μm to about 10 μm .

Heat-resistant inks containing color pigments can be produced by mixing a binder in an amount of about 1 to about 1000 parts by weight, preferably about 10 to about 200 parts by weight, per 100 parts by weight of the color pigment; adding a solvent as needed; and dispersing or kneading the mixture with a dispersion machine, such as a disper, ball mill, roll mill, sand mill, etc., giving a liquid-like or paste-like mixture. Examples of the binder for use in the process are resins, waxes, fats, oils, low-melting glasses (e.g., glass frits such as borosilicate glass, soda glass, etc.), etc. Among these, a heat-resistant ink containing

a color pigment, glass frit, and organic binder is preferable.

Examples of such resins include silicone resins, hydrocarbon resins, vinyl resins, acetal resins, imido resins, amide resins, acrylate resins, polyester resins, polyurethane resins, alkyd resins, protein
 5 resins, cellulose resins, etc. For example, organo polysiloxanes, polymetallo-carbosilanes, polystyrene, polyethylene, polypropylene, polyvinyl acetate, polyvinyl butyral, polyvinyl formal, polyimides, polyamides, poly(meth)acrylates, gelatin, cellulose derivatives, polyvinyl alcohol, polyvinyl pyrrolidone, etc. are mentioned. These can
 10 be used singly or as mixtures or copolymers thereof.

Examples of waxes include paraffin waxes, natural waxes, higher alcohol waxes, higher amide waxes, higher fatty acids, ester waxes, etc. The following examples may be mentioned: paraffin wax, polyethylene wax,
 15 yellow wax, carnauba wax, stearyl alcohol, palmityl alcohol, oleyl alcohol, stearamide, oleamide, palmitamide, ethylenebisstearamide, stearic acid, oleic acid, palmitic acid, myristic acid, ethyl stearate, butyl palmitate, palmityl stearate, stearyl stearate, etc.

Examples of fats and oils are castor oil, soybean oil, linseed oil, olive oil, beef tallow, lard, mineral oils, etc. Examples of
 20 low-melting glasses include glasses with melting points of 70°C or lower, glasses soluble in solvents, and more specifically, a glass frit with the melting point of 700°C or lower and with the particle size of about 0.1 μm to about 100 μm , preferably about 0.2 μm to about 50 μm , water glasses, etc.

The following examples may be mentioned as solvents for use
 25 in the process of dispersion or kneading: aliphatic hydrocarbons such as hexane, octane, decane, cyclohexane, etc.; aromatic hydrocarbons such as benzene, toluene, xylene, cumene, naphthalene, etc.; ketones such as acetone, methyl ethyl ketone, cyclohexanone, etc.; alcohols such as
 30 methanol, ethanol, 2-ethylhexanol, etc.; ethers such as ethylene glycol monomethyl ether, diethylene glycol dibutyl ether, etc.; esters such as methyl acetate, ethyl formate, ethyl acetoacetate, etc.; petroleum distillation fractions such as gasoline, kerosene, gas oil, etc.; water; etc. It is preferable to use such solvents for dilution in an amount
 35 of about 500 parts by weight or less, preferably about 200 parts by weight

or less, per 100 parts by weight of the total amount of the color pigment and binder.

Any patterns, including characters and symbols such as a bar code, may be formed on the heat-resistant label of the invention using the heat-resistant ink composed of such components by known printing methods, laser marking, etc. Examples of printing methods include gravure offset printing, plate offset printing, letterpress printing, intaglio printing, silk screen printing, ink-jet printing, ribbon printing, etc. These printing methods and laser markings may be applied not only when providing the identification part on the label base layer, but also when providing the identification marker directly onto the support.

There is no limitation to the shape of the heat-resistant label of the invention, and a shape suitable for a label attaching machine for attaching the label under high temperature conditions is preferable. The heat-resistant label of the invention can be produced by providing other components (the label base layer, sticking layer, adhering layer, aluminum foil layer, aluminum-alloy foil layer, identification part, etc.) to the support which is formed into a shape suitable for attachment to a product, or by producing a large-scale sheet-like support provided with other components, and then forming the same into a shape suitable for attachment to a product. The forming methods are not limited, and include slit processing, punch processing, etc.

There is no limitation to the label attaching machine for attachment of the heat-resistant label of the invention, and any machine can be used insofar as it can withstand high temperatures. In general, textiles showing little distortion when exposed to high temperatures (preferably, textiles woven in three dimensions) are used for the label-contacting area of the head of the label attaching machine. Examples of fibers for such textiles include Tyranno fiber, carbon fiber, glass fiber, alumina silica fiber, etc., and these can be used singly or in combination. Among these, Tyranno fiber is preferable.

Next, the product of the invention is now described. The product of the invention has the heat-resistant label 1 or 2 of the invention attached, and may be either an intermediate product or a finished product. The heat-resistant labels 1 and 2 of the invention can be adhered to

heat-resistant products at about 300°C to about 1100°C over a short period. The attachment period is usually about 1 second to about 2 minutes, preferably about 1 second to about 1 minute, and more preferably about 1 second to 30 seconds. Any product can be used insofar as the
5 heat-resistant label of the invention can be attached thereto, and the temperature of the product is within the range of from about 300°C to about 1100°C during the product manufacturing process. A heat-resistant label 1 is suitably attached to a product having a temperature in the range from about 300°C to about 670°C. A heat-resistant label 2 is suitably
10 attached to a product having a temperature in the range of from about 300°C to about 1100°C, preferably about 670°C to about 1100°C, and more preferably 700°C to about 1000°C. The product of the invention is usually a metal product, ceramic, glassware, etc. Examples of metal products include primary molded products, such as metal billets of steel, aluminum,
15 stainless steel, copper, etc., slabs, coils, H-shaped steels, cylindrical tubes, rods, plates, etc., and secondary molded products obtained by molding primary molded products by extrusion molding, casting molding, etc.

The label of the invention is heat-resistant, and thus can
20 be attached to a heat-resistant product having high temperatures during a high-temperature treatment or immediately after the treatment. Therefore, product management using the heat-resistant label with barcodes, etc. can be conducted at an earlier stage. Moreover, the present invention can eliminate the necessity of a cooling period, cooling energy,
25 and a cooling place which are required for cooling the heat-resistant products such as metal products, etc. to room temperature so as to attach conventional labels thereon. For example, in production of a stainless steel billet, the heat-resistant label 2 can be attached to a stainless steel billet having a temperature of about 1100°C. During production
30 of an aluminum billet, the heat-resistant label 1 can be attached to the aluminum billet having a temperature of about 650°C immediately after manufacturing.

The label of the present invention can be used for controlling distribution and sales as in conventional bar-code labels, etc., unless
35 the label is not taken off after attachment. In the invention, a product

represents not only commercial products after manufacturing but also rawmaterials, intermediateproducts, etc. during theproductionprocess.

The present invention is now described below in detail with reference to the following Examples but is not limited thereto. Materials

5 used in Experiments and Comparative Experiments are as follows.

<Support>

Aluminum foil: "1N-30-H-40RT",

40 μm thick,

10 produced by Nippon Foil Mfg. Co., Ltd.

Stainless-steel foil: "SUS304 H-TA/MW",

20 μm thick,

produced by Nippon Steel CORP.

15

<Polymetalloccarboxilane resin>

"Tyranno coat VS-100"

produced by Ube Industries, Ltd.

20 "Tyranno coat VN-100"

produced by Ube Industries, Ltd.

<Silicone resin>

"KR255"

25 (straight silicone resin),

produced by Shin-Etsu Chemical Co., Ltd.

"TSR116"

(straight silicone resin),

30 produced by GE Toshiba Silicones.

<Inorganic powder>

"TRNS OXIDE RED AA2005"

(Fe_2O_3),

35 produced by Dainichiseika Color & Chemicals Mfg. Co., Ltd.

<Dispersant>

"Disparlon DA705",

produced by Kusumoto Chemicals, Ltd.

<Heat-resistant ink>

"HF-350A",

produced by General Corporation.

(containing Fe, Cr, Co, polyester resin, and methyl ethyl ketone)

<Aluminum foil layer>

Aluminum foil: "1N-30-H-40RT",

40 μm thick,

produced by Nippon Foil Mfg. Co., Ltd.

<Adhering layer>

Polyisobutylene resin:

"Tetrax 4T",

produced by Nippon Oil Corporation.

 Rubbing tests were conducted by rubbing an sticking layer or a label base layer at a pressure of 0.5 to 1 kg/cm² using 3 to 5 pieces of gauze soaked in xylene. In the rubbing test, when the layer was removed by 5 or 6 rubbings and adhered to the gauze, the layer was defined as a hardened, and when the layer was not removed by 15 rubbings and had barely adhered to gauze, the layer was defined as a cured.

Example 1

 20 parts by weight of Tyranno coat VS-100 as a polymetalloccarbosilane resin, 60 parts by weight of KR-380 as inorganic powder, 0.5 parts by weight of Disparlon DA705 as a dispersant, and 5 parts by weight of xylene as organic solvent were kneaded. Thereafter, the resultant mixture was dispersed at 3000 rpm for 1 hour using a bead mill dispersion machine ("IMZ-2", manufactured by Ashizawa Finetech Ltd.). After confirming the mean particle diameter was 5 μm or less by a grind

gauge, a dispersion mill base M-1 was obtained.

20 g of KR255 as a silicone resin was added to 85.5 g of the dispersion mill base M-1, and subsequently 5 g of xylene was added thereto, followed by kneading. Further, xylene was added to the resultant mixture so as to adjust the viscosity to be 25 to 30 seconds/25°C by viscometer using an I.H.S consistency cup (manufactured by Anest Iwata), to form a coating composition. Subsequently, the coat solution was applied to one side of a 40 μ m thick aluminum foil using a bar coater so that the dry film thickness was 15 μ m, and dried for 10 minutes at 250°C using a convection oven (ASSF-114S, manufactured by Isuzu Seisakusho Co., Ltd.), and then allowed to stand at room temperature. After confirming the resultant coating film was cured by the rubbing test, a support provided with a label base layer was obtained.

In the next process, the coating composition was applied to the other side of the support with a bar coater so that the dry film thickness was 40 μ m, dried at 200°C for 5 minutes using a convection oven (ASSF-114S, manufactured by Isuzu Seisakusho Co., Ltd.), and then allowed to stand at room temperature. After confirming the resultant coating film was hardened by the rubbing test, the coating film was cut into 5 cm x 3 cm pieces, giving heat-resistant labels.

Examples 2 to 13

Heat-resistant labels were prepared using the compositions and under the drying conditions shown in Tables 1 to 3 in the same manner as in Example 1. In Examples 10 to 12, dispersion was conducted at 3000 rpm for 3 hours, and not 1 hour using a bead mill dispersion machine. In Example 13, a hardened coating film (sticking layer) only was formed onto one side of the support, and no cured coating film (label base layer) was formed.

Comparative Examples 1 to 3

Labels that are provided with a sticking layer but are not provided with a label base layer were obtained using the compositions and under the drying conditions shown in Table 4 in the same manner as in Example 1.

Table 1

		Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
Composition of the label I base layer	TYRANNO COAT VS-100	20	30	30	20	20
	TYRANNO COAT VN-100	-	-	-	-	-
	KR255	20	30	-	-	10
	TSR116	-	-	30	20	10
	KR-380	60	30	30	60	60
	TRNS OXIDE RED AA2005	-	-	-	-	-
	DA705	0.5	0.5	0.5	0.5	0.5
	XYLENE	10	7	13	10	10
Drying condition for the label base layer		250°C for 10 minutes				
Composition of the sticking layer		same as the label base layer				
Drying condition for the sticking layer		200°C for 5 minutes				

Table 2

		Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex. 10
Composition of the label I base layer	TYRANNO COAT VS-100	-	-	-	-	-
	TYRANNO COAT VN-100	40	40	30	30	30
	KR255	-	-	10	10	10
	TSR116	-	-	-	10	10
	KR-380	20	60	60	60	-
	TRNS OXIDE RED AA2005	-	-	-	-	60
	DA705	0.5	0.5	0.5	0.5	0.5
	XYLENE	10	10	10	10	10
Drying condition for the label base layer		250°C for 10 minutes				
Composition of the sticking layer		same as the label base layer				same as the label base layer of Ex. 1
Drying condition for the sticking layer		200°C for 5 minutes				

Table 3

		Ex. 11	Ex. 12	Ex. 13
Composition of the label base layer	TYRANNO COAT VS-100	-	-	-
	TYRANNO COAT VN-100	60	30	-
	KR255	20	10	-
	TSR116	20	10	-
	KR-380	-	30	-
	TRNS OXIDE RED AA2005	60	30	-
	DA705	0.5	0.5	-
	XYLENE	10	10	-
Drying condition for the label base layer		250°C for 10 minutes		
Composition of the sticking layer		same as the label base layer of Ex. 6	same as the label base layer of Ex. 10	same as the label base layer of Ex. 10
Drying condition for the sticking layer		200°C for 5 minutes		

Table 4

		Com. Ex. 1	Com. Ex. 2	Com. Ex. 3
Composition of the sticking layer	TYRANNO COAT VS-100	-	-	-
	TYRANNO COAT VN-100	-	-	-
	KR255	60	40	-
	TSR116	-	-	60
	KR-380	30	60	30
	TRNS OXIDE RED AA2005	-	-	-
	DA705	0.5	0.5	0.5
	XYLENE	7	10	13
Drying condition for the sticking layer		150°C for 5 minutes		
Composition of the label base layer		same as the label base layer of Ex. 1		
Drying condition for the label base layer		250°C for 10 minutes		

Test Example 1

The following tests were conducted using the labels obtained in the above-mentioned Examples 1 to 13 and Comparative Examples 1 to 3. The results are shown in Tables 5 and 6.

High temperature label attachment test 1:

Each label was compressed to an aluminum billet at a side with a surface temperature of 500°C at a pressure of 50 g/cm² for 5 seconds using a manually-operated label attaching machine. Thereafter, the

aluminum billet was allowed to cool to room temperature, and was observed for label attachment state, appearance, and scratch resistance. The appearance and scratch resistance of the label of Example 13 were not evaluated since it was not provided with a label base layer. The results are shown in Table 5.

The label adhesion was evaluated according to the following criteria:

o: The label is not peeled off; and

x: The label is peeled off.

The criteria for evaluating the appearance were as follows:

x: The label base layer is partially peeled off the support; and

o: No change observed.

The scratch resistance was evaluated by scratching the label base layer 2 or 3 times at a speed of 5 cm/second using a coin while applying a load of about 500 g to the coin, and the evaluation criteria were as follows:

x: The label base layer crumbled and peeled off the support; and

o: The label base layer is not scratched or the surface of the layer is slightly peeled off.

High temperature label attachment test 2:

Evaluations were conducted in the same manner as in the high temperature label attachment test 1 except that the surface temperature of the label attaching target is 600°C. The results are shown in Table 5.

High temperature label attachment test 3:

Evaluations were conducted in the same manner as in the high temperature label attachment test 1 except that the surface temperature of the label attachment target is 660°C. The results are shown in Table 6.

Table 5

	Attachment test 1 500°C			Attachment test 2 600°C		
	Adhesion	Appearance	Scratch resistance	Adhesion	Appearance	Scratch resistance
Ex. 1	o	o	o	o	o	o
Ex. 2	o	o	o	o	o	o
Ex. 3	o	o	o	o	o	o
Ex. 4	o	o	o	o	o	o
Ex. 5	o	o	o	o	o	o
Ex. 6	o	o	o	o	o	o
Ex. 7	o	o	o	o	o	o
Ex. 8	o	o	o	o	o	o
Ex. 9	o	o	o	o	o	o
Ex. 10	o	o	o	o	o	o
Ex. 11	o	o	o	o	o	o
Ex. 12	o	o	o	o	o	o
Ex. 13	o	-	-	o	-	-
Com. Ex. 1	x	x	x	x	x	x
Com. Ex. 2	x	x	x	x	x	x
Com. Ex. 3	x	x	x	x	x	x

Table 6

	Attachment test 3 660°C		
	Adhesion	Appearance	Scratch resistance
Ex. 1	o	o	o
Ex. 2	o	o	o
Ex. 3	o	o	o
Ex. 4	o	o	o
Ex. 5	o	o	o
Ex. 6	o	o	o
Ex. 7	o	o	o
Ex. 8	o	o	o
Ex. 9	o	o	o
Ex. 10	o	o	o
Ex. 11	o	o	o
Ex. 12	o	o	o
Ex. 13	o	-	-
Com. Ex. 1	x	x	x
Com. Ex. 2	x	x	x
Com. Ex. 3	x	x	x

Example 14

20 parts by weight of Tyranno coat VS-100 as a polymetalloccarboasilane resin, 60 parts by weight of KR-380 as inorganic powder, 0.5 parts by weight of Disparon DA705 as a dispersant, and 5 parts by weight of xylene as organic solvent were kneaded. Thereafter,

the resultant mixture was dispersed at 3000 rpm for 1 hour using a bead mill dispersion machine ("LMZ-2", manufactured by Ajisawa Finetech Ltd.). After confirming the mean particle diameter was 5 μm or less by a grind gauge, a dispersion mill base M-1 was obtained.

- 5 20 g of KR255 as a silicone resin was added to 85.5 g of the dispersion mill base M-1, and subsequently 5 g of xylene was added thereto, followed by kneading. Further, xylene was added to the resultant mixture so as to adjust the viscosity to be 25 to 30 seconds/25°C by viscosity measurement using an I.H.S consistency cup (manufactured by Anest Iwata),
- 10 to form a coating composition. Subsequently, the coating composition was applied with a bar coater to one side of a stainless steel foil 20 μm thick so that the dry film thickness was 15 μm , and dried for 10 minutes at 250°C using a convection oven (ASSF-114S, manufactured by Isuzu Seisakusho Co., Ltd.), and then allowed to cool to room temperature.
- 15 After confirming that the resultant coating film was cured by the rubbing test, a support provided with a label base layer was obtained.

- In the next process, Tetrax 4T was applied as an adhesive with a bar coater to one entire side of an aluminum foil 40 μm thick so that the dry film thickness was 8 μm , and dried at 100°C for 5 minutes
- 20 using a convection oven (ASSF-114S, manufactured by Isuzu Seisakusho Co., Ltd.), and was allowed to cool to room temperature, giving an aluminum foil layer provided with an adhering layer.

- The obtained support with the label base layer, and aluminum foil with the adhering layer, were pasted together. The obtained laminated
- 25 sheet was cut into 5 cm x 3 cm pieces, giving heat-resistant labels.

Examples 15 to 26

- Heat-resistant labels were obtained using the compositions and under the drying conditions shown in Tables 7 to 9 in the same manner as in Example 14. In Examples 23 to 25, dispersion using a bead mill dispersion machine was conducted at 3000 rpm for 3 hours, and not 1 hour.
- 30 In Example 26, only an aluminum foil was formed onto one side of the support with an adhering layer, and a cured coating film (i.e., label base layer) was not formed.

Table 7

		Ex. 14	Ex. 15	Ex. 16	Ex. 17	Ex. 18
Composition of the label base layer	TYRANNO COAT VS-100	20	30	30	20	20
	TYRANNO COAT VN-100	-	-	-	-	-
	KR255	20	30	-	-	10
	TSR116	-	-	30	20	10
	KR-380	60	30	30	60	60
	TRNS OXIDE RED AA2005	-	-	-	-	-
	DA705	0.5	0.5	0.5	0.5	0.5
	XYLENE	10	7	13	10	10
Drying condition of the label base layer		250°C for 10 minutes				
Structure of the adhering layer		adhering layer and aluminum foil				

Table 8

		Ex. 19	Ex. 20	Ex. 21	Ex. 22	Ex. 23
Composition of the label base layer	TYRANNO COAT VS-100	-	-	-	-	-
	TYRANNO COAT VN-100	40	40	30	30	30
	KR255	-	-	10	10	10
	TSR116	-	-	-	10	10
	KR-380	20	60	60	60	-
	TRNS OXIDE RED AA2005	-	-	-	-	60
	DA705	0.5	0.5	0.5	0.5	0.5
	XYLENE	10	10	10	10	10
Drying condition of the label base layer		250°C for 10 minutes				
Structure of the adhering layer		adhering layer and aluminum foil				

Table 9

		Ex. 24	Ex. 25	Ex. 26
Composition of the label base layer	TYRANNO COAT VS-100	-	-	-
	TYRANNO COAT VN-100	60	30	-
	KR255	20	10	-
	TSR116	20	10	-
	KR-380	-	30	-
	TRNS OXIDE RED AA2005	60	30	-
	DA705	0.5	0.5	-
	XYLENE	10	10	-
Drying condition of the label base layer		250°C for 10 minutes		
Structure of the adhering layer		adhering layer and aluminum foil		

Test Example 2

The following tests were conducted using the labels obtained in the above Examples 1, 14 to 26, and Comparative Examples 1 to 3.

High temperature label attachment test 4:

5 Testing was conducted in the same manner as in the high temperature label attachment test 1 except that the surface temperature of the label attachment target was 680°C. The appearance was evaluated and those labels showing slight cracking were rated as "A". The results are shown in Table 10.

10

High temperature label attachment test 5:

 Testing was conducted in the same manner as in the high temperature label attachment test 1 except that the surface temperature of the label attachment target was 700°C. The label of Example 1 was
15 not evaluated. The results are shown in Table 10.

High temperature label attachment test 6:

 Testing was conducted in the same manner as in the high temperature label attachment test 1 except that the surface temperature of the label attachment target was 1000°C. The label of Example 1 was
20 not evaluated. The results are shown in Table 11.

Table 10

	Attachment test 4 680°C			Attachment test 5 700°C		
	Adhesion	Appearance	Scratch resistance	Adhesion	Appearance	Scratch resistance
Ex. 1	o	Δ	o	-	-	-
Ex. 14	o	o	o	o	o	o
Ex. 15	o	o	o	o	o	o
Ex. 16	o	o	o	o	o	o
Ex. 17	o	o	o	o	o	o
Ex. 18	o	o	o	o	o	o
Ex. 19	o	o	o	o	o	o
Ex. 20	o	o	o	o	o	o
Ex. 21	o	o	o	o	o	o
Ex. 22	o	o	o	o	o	o
Ex. 23	o	o	o	o	o	o
Ex. 24	o	o	o	o	o	o
Ex. 25	o	o	o	o	o	o
Ex. 26	o	-	-	o	-	-
Com. Ex. 1	x	x	x	x	x	x
Com. Ex. 2	x	x	x	x	x	x
Com. Ex. 3	x	x	x	x	x	x

Table 11

	Attachment test 6 1000°C		
	Adhesion	Appearance	Scratch resistance
Ex. 14	o	o	o
Ex. 15	o	o	o
Ex. 16	o	o	o
Ex. 17	o	o	o
Ex. 18	o	o	o
Ex. 19	o	o	o
Ex. 20	o	o	o
Ex. 21	o	o	o
Ex. 22	o	o	o
Ex. 23	o	o	o
Ex. 24	o	o	o
Ex. 25	o	o	o
Ex. 26	o	-	-
Com. Ex. 1	x	x	x
Com. Ex. 2	x	x	x
Com. Ex. 3	x	x	x

Claims

1. A composition for a heat-resistant label comprising a polymetallocarbosilane resin (A), a silicone resin (B), and a solvent (C), wherein the polymetallocarbosilane resin (A) and the silicone resin (B) are mixed in a weight ratio of about 1 to about 9 to about 9 to about 1.
5
2. A composition for a heat-resistant label further comprising an inorganic powder (D) in an amount of about 0.0001 to about 80% by weight.
10
3. A composition for a heat-resistant label according to Claim 1 or 2, wherein the polymetallocarbosilane resin (A) and the silicone resin (B) are mixed in a weight ratio of about 3 to about 7 to about 8 to about 2.
15
4. A composition for a heat-resistant label according to any one of Claims 1 to 3, wherein the weight-average molecular weight of the polymetallocarbosilane resin (A) is about 500 to about 10000.
20
5. A composition for a heat-resistant label according to any one of Claims 1 to 4, wherein the weight-average molecular weight of the silicone resin (B) is about 200 to about 5000000.
25
6. A composition for a heat-resistant label according to any one of Claims 1 to 5, wherein the polymetallocarbosilane resin (A) is at least one member selected from the group consisting of polytitanocarbosilane resins and polyzirconocarbosilane resins.
30
7. A heat-resistant label comprising a support and a sticking layer, the sticking layer being obtained by applying a composition of any one of Claims 1 to 6 onto one side of the support and evaporating the solvent contained in the composition to form a hardened coating film.
35
8. A heat-resistant label according to Claim 7, wherein the sticking layer is about 5 μm to about 100 μm thick.

9. A heat-resistant label according to Claim 7 or 8, wherein the support is about 5 to about 100 μm thick.
10. A heat-resistant label according to any one of Claims 7 to 9, wherein the support is any one of an aluminum foil, stainless steel foil, or copper foil.
11. A heat-resistant label according to any one of Claims 7 to 10 having a heat-resistant label base layer on the other side of the support.
12. A heat-resistant label according to Claim 11, wherein the label base layer is about 0.5 μm to about 100 μm thick.
13. A heat-resistant label according to Claim 11 or 12, wherein the label base layer is a cured coating film obtained by crosslinking the resins of the composition of any one of Claims 1 to 6.
14. A heat-resistant label according to any one of Claims 11 to 13 comprising an identification part on the label base layer.
15. An article to which a heat-resistant label of any one of Claims 7 to 14 is attached using a cured sticking layer.
16. A method for producing a heat-resistant label, the method comprising the steps of:
- applying a composition of any one of Claims 1 to 6 to one side of a support; and
 - drying the applied composition to form a hardened coating film.
17. A production method according to Claim 16, wherein the applied composition is dried at about 50°C to about 240°C.
18. A production method according to Claim 16 or 17, comprising, prior to the step of applying a composition of any one of Claims 1 to 6 to

one side of a support, the steps of:

- applying a composition for a heat-resistant label base layer to the other side of the support; and
- drying the applied composition to form a cured coating film.

5

19. A production method according to any one of Claims 16 to 18, wherein the composition for a label base layer is a composition of any one of Claims 1 to 6.

10 20. A method for producing an article with a heat-resistant label attached, the method comprising the step of attaching a heat-resistant label of any one of Claims 7 to 14 to an article at about 300°C to about 670°C.

15 21. A heat-resistant label comprising a support and an aluminum foil layer or aluminum-alloy foil layer being laminated on one side of the support.

20 22. A heat-resistant label according to Claim 21, wherein the aluminum foil layer or aluminum-alloy foil layer is laminated on the support through an adhering layer.

23. A heat-resistant label according to Claim 21 or 22, wherein the aluminum foil layer or aluminum-alloy foil layer has a thickness of 5 μm to 100 μm .

25

24. A heat-resistant label according to any one of Claims 21 to 23, wherein the support is a stainless steel foil, copper foil, or iron foil.

30 25. A heat-resistant label according to any one of Claims 21 to 24, comprising a heat-resistant label base layer on the other side of the support.

26. A heat-resistant label according to Claim 25, wherein the label base layer has a thickness of about 0.5 μm to about 100 μm .

35

27. A heat-resistant label according to Claim 25 or 26, wherein the label base layer is a cured coating film obtained by crosslinking the resins of a composition of any one of Claims 1 to 6.

5 28. A heat-resistant label according to any one of Claims 25 to 27, comprising an identification part on the label base layer.

29. An article to which a heat-resistant label of any one of Claims 21 to 28 is attached.

10

30. A method for producing an article with a heat-resistant label attached, the method comprising the step of attaching a heat-resistant label of any one of Claims 21 to 29 to an article at about 300°C to about 1100°C.

Abstract

The present invention relates to compositions for heat-resistant labels that are attachable at temperatures of from 300°C to 1100°C, heat-resistant labels, products with the labels attached, and methods for producing the labels. The heat-resistant labels having as an adhesive layer a hardened coating film made of a composition containing a polymetalloccarboxilane resin (A), a silicone resin (B), a solvent (C), and, as needed, an inorganic powder (D), can be attached under high temperature conditions. More specifically, the present invention relates to compositions for heat-resistant labels comprising the polymetalloccarboxilane resin (A), the silicone resin (B), and the solvent (C), with the polymetalloccarboxilane resin (A) and the silicone resin (B) being mixed in a weight ratio of about 1 to about 9 to about 9 to about 1; heat-resistant labels composed of the composition, and products with the labels attached.